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A helicopter view of microwave application to chemical processes: reactions, separations, and equipment concepts

Abstract: We present a helicopter view of microwave technology application to various reaction and separation processes, including liquid-phase organic syntheses, gas-solid catalytic reactions, polymerizations, extraction, distillation, crystallization, membrane separation, and adsorbent regeneration/dehydration. The overarching aim is to demonstrate the breadth of potential applications of microwave technology to chemical industry, with particular attention to separations, as this is a less explored microwave application area. In this context, some key findings, opinions, and developments in the relevant literature are summarized. In addition, the present microwave equipment concepts for chemical processes are critically reviewed and new ones are put forward, as we believe that an important milestone in the road from laboratory-scale microwave experimentation to industrial-scale microwave-assisted chemical processing is the design and development of innovative microwave equipment concepts tailored for specific chemical processes.

Keywords: microwaves; process intensification; reactions; separations.

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1 Introduction

1.1 Energy aspect of process intensification

Process intensification (PI) is commonly seen as one of the most promising development paths for the chemical process industry and one of the most important progress areas for modern chemical engineering.

For more than two decennia, PI has been merely considered as a kind of technological "toolbox" containing some spectacular examples of process improvement. Also, the three books on PI published so far (Stankiewicz and Moulijn 2003, Keil 2007, Reay et al. 2008) describe PI as a bundle of diverse technologies. In their review article, Van Gerven and Stankiewicz (2009) proposed a fundamental view on PI. They defined four basic principles and four domains: spatial, thermodynamic, functional, and temporal, which need to be addressed in order to intensify a chemical process. The thermodynamic domain focuses primarily on energy. The basic question here is how energy can be transferred from the source to the recipient in the required form, in the required amount, at the required moment, and at the required position. All energy that does not fit the requirements (unable to be absorbed, more than needed, "wrong" form, too early or too late, too far away) is not used optimally and (partly) dissipates. The conventional input of energy in chemical processing systems occurs via conductive heating with a steam boiler as a typical heat source. Yet, there exist a large variety of other forms of energy that can be applied for PI. The examples here include ultrasound (for reactions or crystal nucleation), light (in photocatalysis), electric fields (in extraction or for orientation of molecules), or microwaves.

Microwave (dielectric) heating of materials has been known for a long time, and the development of microwave ovens has more than 60 years of history. The classic publications by Gedye et al. (1986, 1988) opened a period of very intensive investigations of microwave effects on chemical reactions in homogeneous systems. Since then, hundreds of research papers have been published, and research has expanded also toward heterogeneous catalysis and separation systems. The present paper gives an overview of microwave technology application to various reaction and separation processes. In addition, the present microwave equipment concepts for chemical processes are critically reviewed and new ones are put forward. It is stressed that the aim is to present not a detailed review but rather a helicopter view on these areas summarizing some key findings, opinions, and developments in the relevant literature.

1.2 Microwaves

Microwaves are a form of electromagnetic radiation situated between the radio and the infrared frequencies, that is, between 300 MHz and 300 GHz, which corresponds to wavelengths in vacuum of about 1 m to 1 mm. Due to legislation, the most common frequencies available for chemical processes are 915 MHz, 2.45 GHz, and 5.85 GHz.

In liquid systems, molecules that have a permanent dipole moment (e.g., water) can rotate in the presence of a rapidly alternating electric field of microwave radiation. Similarly, ions are subjected to rapid translational movements (Figure 1). As a result of the rotational or translational motion, "internal friction" occurs in the polar medium, resulting in heating of the medium.

Microwave heating of liquids is therefore fundamentally different from the conventional conduction-based heating and is often called "volumetric heating." It is attractive from the PI point of view since it is not limited by factors such as the specific heat transfer surface or the heat transfer coefficient. Ideally, one could also expect microwave heating to be gradientless, although it is never the case in reality.

Solid materials can be divided into three categories with regard to their interaction with microwaves (Figure 2). Conductors, such as metals or graphite, reflect microwaves from their surface. In insulators, such as polypropylene or quartz glass, microwaves penetrate the material, while, in the so-called "dielectric lossy materials," such as silicon carbide, they are absorbed, resulting in heat generation.

The properties of any material with respect to microwave radiation are described by its complex permittivity, $\varepsilon^{\star}$, and complex permeability, $\mu^{\star}$.

$$\varepsilon^{*}=\varepsilon'\text{-}j\varepsilon''=\varepsilon_{0}(\varepsilon'_{r}\text{-}j\varepsilon''_{eff}) \tag{1}$$

$$\mu^{*}=\mu'\text{-}j\mu'' \tag{2}$$

The real part (ε') of the relative permittivity (i.e., the dielectric constant) characterizes the ability of the material to store electrical energy, whereas the imaginary part (ε'') is the loss factor that reflects the ability of the material to dissipate electrical energy. Similarly, the real part of the complex permeability (μ') represents the amount of magnetic energy stored within the material, while the imaginary part (μ'') represents the amount of magnetic energy, which can be converted into thermal energy. The ratios between the imaginary and the real parts of the permittivity and permeability are called loss tangent ($\tan\delta$) and magnetic loss tangent ($\tan\delta_{\mu}$), respectively.

$$\tan\delta=\frac{\varepsilon''}{\varepsilon'} \tag{3}$$

$$\tan\delta_{\mu}=\frac{\mu''}{\mu'} \tag{4}$$

The values of ε', ε'', and $\tan\delta$ for some exemplary materials are shown in Table 1.

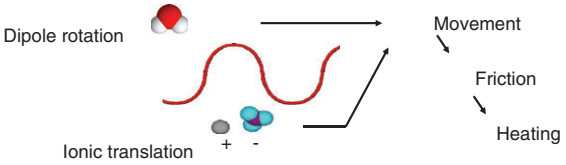

Figure 1 Mechanisms of liquid heating by microwaves.

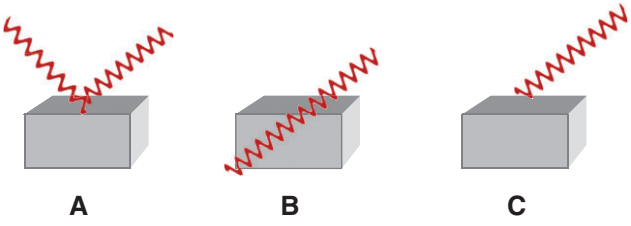

Figure 2 Microwave interactions with different types of materials: (A) conductive material, (B) insulating material, and (C) absorbing material.
Reproduced with permission from Durka et al. (2009).

Table 1 Dielectric constant (ε'), dielectric loss (ε''), and loss tangent ($\tan\delta$) of common materials at 25°C.

Material	Dielectric constant ε'	Dielectric loss ε''	Loss tangent $\tan\delta$
Vacuum	1.00	0	0
Air	1.0006	0	0
Water	80.4	9.89	0.123 (2.45 GHz)
Methanol	32.6	21.48	0.659 (2.45 GHz)
Ethanol	24.3	22.86	0.941 (2.45 GHz)
Glass (Pyrex)	4.82	0.026	0.0054 (3 GHz)
Styrofoam	1.03	0.0001	0.0001 (3 GHz)
PTFE	2.08	0.0008	0.0004 (10 GHz)
Titanium dioxide	50	0.25	0.005
Zirkonia	20	2	0.1
Zinc oxide	3	3	1
Magnesium oxide	9	0.0045	0.0005
Aluminum oxide	9	0.0063	0.0007

Information can be found in Pozar (1998) and Hayes (2002).

The frequency dependence of ε' and ε'' is described by the Debye equation, for example (Mingos and Whittaker 1997):

$$\varepsilon'=\varepsilon'_{\infty}+\frac{(\varepsilon'_0-\varepsilon'_{\infty})}{(1+\omega^2\tau^2)} \tag{5}$$

$$\varepsilon''=\frac{(\varepsilon'_0-\varepsilon'_{\infty})\omega\tau}{(1+\omega^2\tau^2)} \tag{6}$$

where ε'_0 is the static dielectric constant, ε'_{∞} is the high frequency constant, ω is the angular frequency ($\omega=2\pi f$), and τ is the relaxation time characterizing the rate of buildup and decay of polarization. In liquids, dipoles are randomly oriented and orientation changes continuously due to thermal motions; therefore, the relaxation time is defined by the following expression:

$$\tau=\frac{4\pi r^3\mu}{kT} \tag{7}$$

where r is the radius of the dipole, μ is the dynamic viscosity, k is the Boltzmann's constant, and T is the temperature.

For an ideal solid in which each dipole has a number of equilibrium positions, the relationship between τ and dielectric constant may be derived from Boltzmann statistics:

$$\tau=\frac{e^{U_a/kT}(\varepsilon'_0+2)}{\mu\left(\varepsilon'_{\infty}+2\right)} \tag{8}$$

where U_a is the potential barrier separating dipole positions.

Microwaves can penetrate into a material up to a certain depth, called the penetration depth (D_p). This is usually described as the depth where the microwave power drops to about 37% of the initial value. For materials where $\varepsilon''/\varepsilon'<1$ (lossy dielectrics), D_p can be described as follows:

$$D_p=\frac{\lambda}{2\pi}\frac{\sqrt{\varepsilon'}}{\varepsilon''} \tag{9}$$

where λ is the wavelength.

The average power dissipated in a material volume V can be expressed as

$$P=\omega\varepsilon_0\varepsilon''E^2_{rms}V+\omega\mu_0\mu''H^2_{rms}V \tag{10}$$

where E_{rms} is the root mean square of the electric field intensity, H_{rms} is the root mean square of the magnetic field intensity, ω is the angular frequency, and ε_0 and μ_0 are the permittivity and permeability in free space, respectively.

1.3 Basic microwave equipment

The microwave equipment (also frequently called "applicators") used in chemical processing can be divided into three basic categories: the multimode, the mono (or single)-mode, and the traveling-wave devices.

The multimode applicators are the most widespread ones, with applications starting from domestic ovens up to large-scale industrial dryers. They usually have the form of a rectangular closed metal box (called "cavity"; Figure 3) – a Faraday cage that has at least two dimensions longer than half of the wavelength. Inside the cavity, a large number of resonance modes exist as the microwaves get reflected from the cavity walls. Owing to these reflections, wave interference occurs. Therefore, the microwave field, which the heated material (load) is subjected to, is highly nonuniform regardless of the application of a mode stirrer or a rotating disk to support the load. The advantage of these applicators, however, is that they can be made large to accommodate sizable volumes of materials for processing.

In contrast with the multimode applicators, in the monomode applicators, a relatively more stable single-standing wave is generated inside the cavity. The irradiated material is usually placed in one of the maxima of the electromagnetic field (Figure 4). This distinguishing feature of monomode applicators entails that their volume and the material load are strictly limited in size. Therefore, monomode applicators are usually implemented to process volumes up to 200 ml, which can be considered their main limitation. However,

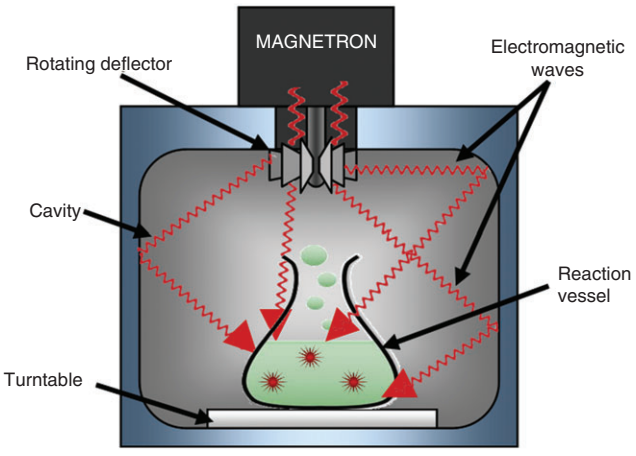

Figure 3 Multimode microwave applicator.

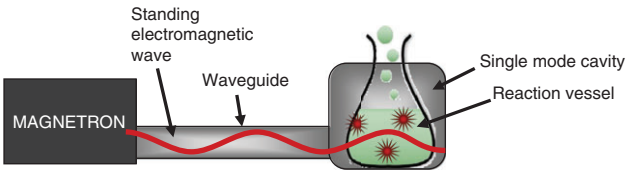

Figure 4 Monomode microwave applicator.

the advantage of the single-mode cavities, compared to multimode ones, is that higher electromagnetic field densities can be developed inside the cavity and thus higher heating rates. Although the electromagnetic field pattern is well defined inside an empty single-mode cavity, it may change drastically in the presence of the heated material inside the cavity (Ondruschka et al. 2012).

A microwave field does not need to be resonant. In contrast with cavity-based applicators, traveling-wave applicators support a microwave field propagating in a single direction from the inlet to the outlet of a waveguide. Traveling-wave applicators of various configurations can be considered. In Figure 5, a schematic representation of a traveling-wave applicator of meander type is displayed (adapted from Meredith 1998).

1.4 "Traditional" industrial applications of microwaves

Microwave (pre)heating finds its applications in several sectors of process industry:

- Rubber and plastic industry (preheating of resins and rubbers, vulcanization, bonding, curing, welding, shrinking)
- Food industry (drying, cooking, tempering, pasteurization, sterilization, thawing)

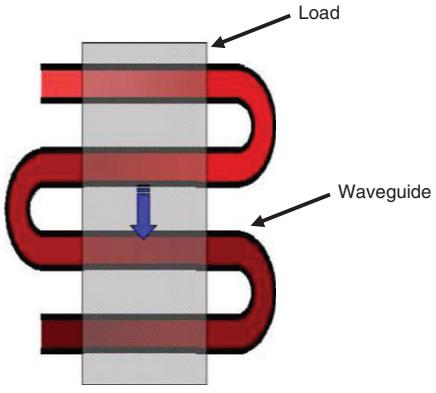

Figure 5 Schematic representation of a traveling-wave applicator of meander type.
The concept was presented in Meredith (1998).

- Pharmaceutical industry (vacuum drying)
- Ceramics (drying, joining, sintering)
- Paper and wood (drying, gluing)
- Textile (drying, dye fixation, control of moisture content)

Equipment used in those applications includes primarily large-scale multimode microwave chamber furnaces equipped with belt or roller conveyors (continuous operation) or racks (batch operation). The most important advantages of microwave heating in these applications are cost and energy savings, shorter processing times, space savings, and better product quality (due to faster processing in milder conditions; reduced breakage in ceramic products due to absence of thermal gradients). Table 2 lists some selected publications where more detailed information on traditional industrial microwave applications can be found.

2 Microwave-assisted reaction systems

2.1 Liquid-phase reactions (organic synthesis)

The literature concerning the enhancement effects of microwaves on chemical reactions in general and homogeneous liquid-phase organic reactions, in particular, is exceptionally rich, and there exist several good reviews on this subject (Lidstrom et al. 2001, Hajek 2002, Hayes 2002, Larhed et al. 2002, Kappe 2004, Leadbeater et al. 2004, Nuchter et al. 2004, Dallinger and Kappe 2007, Kappe and Dallinger 2009, Kappe and Van der Eycken 2010, Bag et al. 2011, Mehtaa and Van der Eycken 2011, McBurney et al. 2012, Gupta et al. 2013, Kranjc and Kocevar 2013a,b). The authors generally agree about the ability of microwave heating to accelerate the organic reactions and acceleration factors from several to more than 1000 are reported. Several examples of reactions accelerated by microwave heating are given in Table 3. One can see that not only the rate of the process is affected but also the product yield, which in some cases increases as a result of microwave heating.

Moreover, several papers on the use of microwaves in continuous-flow capillary reactors or microreactors have been published. He et al. (2004) and Comer and Organ (2005) reported rate enhancements, higher yields, and greater product selectivity for Suzuki cross-coupling

Table 2 Selected publications on traditional applications of microwaves.

Publication	Publication type	Applications discussed
Osepchuk 2002	Review	Various, including preheating and vulcanizing of rubber, sintering and synthesis of ceramics, pasteurization, sterilization, waste remediation
Schubert and Regier 2005	Book	Various, from baking and drying to blanching, thawing, and tempering. Covers the key area of process measurement and control to ensure more uniform heating of food products
Vadivambal and Jayas 2010	Review	Heating of food
Li et al. 2011	Review	Drying
Datta and Anantheswaran 2001	Book	Food processing
Ahmed and Ramaswamy 2007	Review	Food pasteurization and sterilization
Ishii 1995	Review	Various, including curing, drying, heating, pasteurization
Haghi 2005	Review	Textile processing
Sanga et al. 2000	Review	Drying
Riedhammer 1998	Review	Ceramic processing
Kudra and Mujumdar 2009	Book	Drying
Duan et al. 2010	Review	Microwave-assisted freeze-drying of foods
Zhang et al. 2006	Review	Drying of fruits and vegetables

Table 3 Effect of microwave heating on reaction time and product yield for several exemplary reactions (Gedye et al. 1988, Larhed et al. 2002, Johnstone et al. 2010).

Reaction	Reaction time		Product yield	
	Conventional	Microwave	Conventional	Microwave
Hydrolysis of benzamide to benzoic acid	1 h	10 min	90%	99%
Oxidation of toluene to benzoic acid	25 min	5 min	40%	40%
Esterification of benzoic acid with methanol	8 h	5 min	74%	76%
S_N2 reaction of 4-cyanophenoxide ion with benzyl chloride	16 h	4 min	89%	93%
Heck arylation of olefines	20 h	3 min	68%	68%
Ruthenium catalyzed reaction of endo norbornene imide with dimethyl acetylenedicarboxylate (cycloaddition)	60 min	2 min	84%	93%

reactions carried out in capillary reactors. Jachuck et al. (2006) investigated the influence of microwave intensity and residence time on the oxidation of benzyl alcohol to benzaldehyde performed in a continuous microchannel reactor. The authors found microwave irradiation to accelerate the reaction rate (up to ~10 times) and claimed to have observed an unexplained nonthermal microwave effect. Besides, microwave chemistries in continuous-flow microreactor devices are a promising concept to address the limitation of scalability of laboratory-scale microwave chemistries to production-scale processes. A recent good work on this subject has been published by Glasnov and Kappe (2011).

The origin of some positive microwave effects such as those mentioned earlier and, more general, the thermochemical mechanisms via which microwaves influence chemical reactions have been a subject of a long-standing debate in the microwave community. Among other things, microscopic hot-spots, molecular agitation, and the improved transport properties of molecules have been postulated as potential reasons of enhanced activation (Jacob et al. 1995). In addition, other effects, such as the positioning of the transition states or decrease in the activation energy in the Arrhenius law, have been hypothesized (Perreux and Loupy 2001, 2002, Howarth and Lockwood 2004, de la Hoz et al. 2005). Nowadays, more and more authors agree that the effect of microwaves has a purely thermal character (Lidstrom et al. 2001, Kuhnert 2002, Kappe 2004). Stuerga and Gaillard (1996b,c) studied theoretically the existence of nonthermal microwave effects from a thermodynamic point of view and concluded that there is "no doubt that electric field cannot have any molecular effects." In more recent papers, Obermayer et al. (2009) and Kappe et al. (2013)

discuss the influence of such factors as the material of the vessel, in which experiments are carried out, and the type of the temperature measuring device used. We generally share the view of Kappe and his coworkers regarding the thermal effects of microwaves and the importance of the method for measuring the reaction temperature. Based on our own experimental work (see next section), we may assume that many of the "unexplained, nonthermal" microwave effects reported in the past resulted from incorrect or insufficient temperature measurements in the system.

Finally, it should be remarked that many organic reactions could proceed faster to increased product yields when the heating (and cooling) rate is increased irrespective of the heating method. In this regard, the application of microwaves is advantageous compared to the conventional method. A good paper on this matter has been published by Strauss and Rooney (2010), where the authors suggest the following rule of thumb for synthetic reactions: "thermal reactions proceed optimally when they are rapidly heated to the highest tolerable temperature, held there for the shortest possible time and then quenched."

2.2 Heterogeneous catalytic gas-phase reactions

In gas-solid heterogeneous catalytic systems, hot-spot formation and selective heating are primarily considered to be the mechanisms responsible for the enhanced rate of reaction, while selective heating and superheating are mainly postulated in homogeneous systems. Hot-spots are places inside the catalytic bed where the temperature is considerably higher than the average temperature; hence, reaction occurs at a much higher rate (Bond et al. 1993, Chen and Spiro 1995, Zhang et al. 2001, 2003a). Very often, the existence of this phenomenon is explained by the nonhomogenous distribution of the electromagnetic field inside the catalytic bed. Sizes of hot-spots are in the range of 90–1000 μm and temperatures can be 100–200 K higher than the bulk temperature of the catalytic bed (Zhang et al. 1999). Obviously, the microscale nature of this phenomenon induces technical problems with measuring the temperature of hot-spots by the available techniques; hence, an experimental proof of their existence is lacking. Nevertheless, even when measuring temperature with the best currently available method (i.e., fiber optics), very significant differences can be noticed in a catalyst bed. Figure 6 presents the axial temperature profile in a small (2.5 g) sample of Rh/CeO_2-ZrO_2 catalyst under nonreacting conditions (Durka et al. 2009). On a 10 mm length, the temperature difference exceeded 50°C. It is also worth noting that the simultaneous measurements done with the infrared sensor did not indicate any gradients, as the sensor measures temperature only at the outside surface of the vial in which the catalyst was held. This again indicates the importance of the proper choice of the measurement method and instrument when dealing

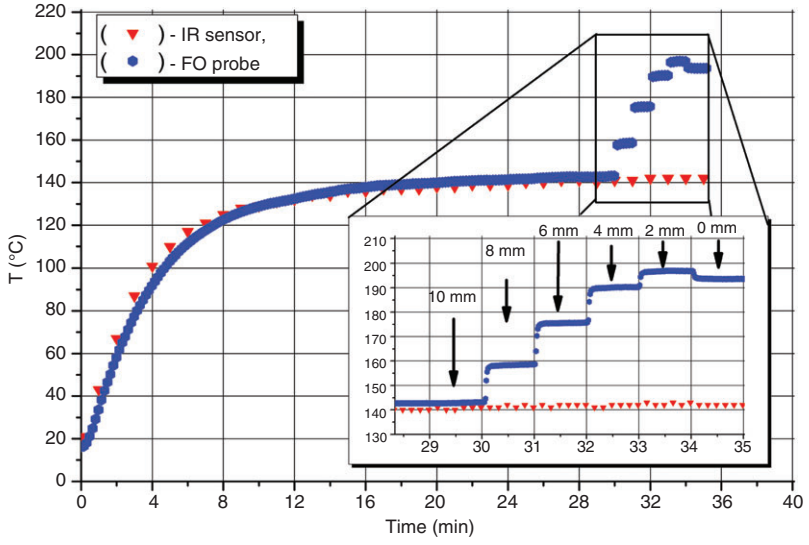

Figure 6 Axial temperature distribution inside 2.5 g Rh/CeO_2-ZrO_2 sample. Reproduced with permission from Durka et al. (2009).

with microwaves. This problem has been discussed in more detail by Durka et al. (2010).

Selective heating in gas-solid systems appears in two forms that may occur simultaneously. The first form is the selective heating of a catalyst particle while the gas phase remains at lower temperature. This form of selective heating was proposed by Roussy et al. (1994) as the probable reason of the observed enhanced selectivity toward higher hydrocarbons in a microwave field. The second form is the development of the temperature difference between the nanoparticles of metal catalyst and the support material. It is known that metal particles can be heated up very rapidly to high temperatures by microwave irradiation. The required metal particle size has to be smaller or equal to the penetration depth, which for most metals is in the range of 1–10 μm at 2.45 GHz (Gupta and Wong Wai Leong 2007). This phenomenon is considered by some researchers to be responsible for the observed higher reaction rate and higher selectivity of products formed (Thiebaut et al. 1983, 1993, Seyfried et al. 1994, Stuerga and Gaillard 1996a, Roussy et al. 1997a, Chemat et al. 1998, Chemat-Djenni et al. 2007). However, this hypothesis is also contested. Perry et al. (1997a,b) presented results from their experimental and theoretical work, which deny the existence of a temperature difference between the active sites of catalyst and its support.

Some additional important works in the area of microwave-assisted heterogeneous catalysis are presented in Table 4.

2.3 Polymerization reactions

The literature concerning the effects of microwaves on polymerization reactions and polymer processing is rich, and there exist good reviews and books on that topic (Bogdal et al. 2003, Wiesbrock et al. 2004, Bogdal and Prociak 2007a,b, Hoogenboom and Schubert 2007, Zhang et al. 2007, Ebner et al. 2011). The reactions investigated include the following:

- Free-radical polymerizations (e.g., methacrylates)
- Controlled radical polymerizations
- Emulsion polymerizations (e.g., polystyrene)
- Ring-opening polymerizations (e.g., polyoxazolines)
- Step-growth polymerizations
  - Synthesis of aramides, polyamides, polymides, and polyimide-silica hybrid materials
  - Synthesis of polyesters and polyethers
  - Synthesis of epoxy resins
  - Synthesis of polyurethanes

The most important reported effect of microwaves on these reactions is the increased speed of processing. The microwave-assisted reactions proceed much faster than by conventional heating and the differences in reaction rates reach orders of magnitude. For instance, Correa et al. (1998) reported ~70 times acceleration of the emulsion polymerization of styrene. Another effect reported is the microwave-assisted synthesis of polymers with different molecular weights compared to those obtained by conventional heating. The above-cited authors (Correa et al. 1998) reported the molecular weight of polystyrene prepared with microwaves to be 1.2 times higher than the one obtained with the conventional method. In Figure 7, a molecular weight-versus-time curve for the direct polyesterification of butane-1,4-diol with succinic acid is shown by Velmathi et al. (2005). One clearly sees that not only the microwave-assisted process is much faster than the conventional one, but also approximately two times higher molecular weights are achieved with microwaves compared to conventional heating. Those claims, however, are contradicted by our own research work (Komorowska et al. 2009), where noncatalyzed and tin(II) chloride-catalyzed polyesterification of adipic acid with neopentyl glycol reaction was investigated using microwave and conventional heating in an open, stirred vessel under a nitrogen atmosphere. Except for faster heating times obtained under microwave heating, no different effects on the polyesterification reaction itself were found between the two heating modes. Research experience so far has shown that whether microwave irradiation can intensify a polymerization reaction depends on the nature of the chemical system and the processing conditions. Some very recent examples of different types of polymerization that were intensified under microwave irradiation, in terms of process acceleration or increased molecular weight, are discussed by Yamada et al. (2013) (ring-opening polymerization), Choi et al. (2013) (polycondensation), and Adlington et al. (2013) (catalytic chain transfer polymerization).

In free-radical polymerizations, microwaves were shown to increase the selectivity to the required product. An example here is shown in Figure 8, where the use of microwaves changed the selectivity in the synthesis of (methyl)acrylamides (Hoogenboom and Schubert 2007). In addition, a different particle size distribution in styrene polymerization was reported as a result of microwave heating (see Figure 9) (Xu et al. 2005).

Other interesting polymer-related processes studied in the literature include the rapid depolymerization of polyamide-6 (carpet recycling) (Klun and Krzan 2000) and the rapid curing of polyurethane (Jullien and Valot 1985) and epoxy resin (Degamber and Fernando 2004).

Table 4 Observed effects on gas-solid catalytic reactions carried out under the presence of microwave irradiation and their possible explanation.

Application	Observed effect	Explanation of observed effects	References
Methane decomposition	Higher selectivity	Nonuniform temperature conditions	Ioffe et al. 1995
	No comparison with conventional process	N/A	Tse et al. 1990, Wan et al. 1990, Pollington et al. 1995
	Higher conversion	No explanation	Cooney and Xi 1996b
	Higher conversion, higher selectivity,	Plasma formation, arcing	Zhang et al. 2003c
	Higher conversion	Microplasmas generated by N_2 gas	Fidalgo et al. 2008b
Methane oxidation	No comparison with conventional process	N/A	Tse et al. 1990, Wan 1993, Roussy et al. 1994, 1997b
	Higher conversion, higher selectivity, reduction in reaction temperature	Hot-spot formation	Bi et al. 1999
	No effects	N/A	Zhang et al. 2003c
	Reduction of reaction temperature	Hot-spot formation	Bond et al. 1993, Chen et al. 1995, 1997
Methane oligomerization	No comparison with conventional process	N/A	Marun et al. 1999, Conde et al. 2001
Methane dry reforming	Higher conversion, higher selectivity	Hot-spot formation	Zhang et al. 2003b
	Higher conversion	Microplasmas formation	Fidalgo et al. 2008a, 2011
Methane synthesis	No comparison with conventional process	N/A	Wan et al. 1991, Wan 1993
HCN synthesis	Higher selectivity	Selective catalyst heating	Koch et al. 1997
H_2S decomposition	Higher conversion	Hot-spot formation	Zhang et al. 1999
NOx, SO_2 reduction	Higher conversion	No explanation	Tse et al. 1990, Cha 1994, Cha and Kong 1995, Kong and Cha 1995, Wang et al. 2000, Wei et al. 2011
	Enhanced reaction rate		
SO_2 reduction	Higher conversion	Hot-spot formation	Zhang et al. 2001
	Phase transition of catalyst		
CO oxidation	Higher rate	Imprecise temperature measurement	Perry et al. 1997b
	No effects	N/A	Silverwood et al. 2006, 2007,
Propane oxidation	Negligible effect	N/A	Will et al. 2003, 2004, Krech et al. 2008
	Higher conversion, reduction in reaction temperature	Hot-spot formation	Beckers et al. 2006
Ethane/ propane/n-butane dehydrogenation	No comparison with conventional process	N/A	Cooney and Xi 1996a
Ethane dehydrogenation	Higher conversion[a]	Phase transition of catalyst	Sinev et al. 2009
o-Xylene/toluene oxidation	Higher conversion, higher selectivity	Hot-spot formation More homogeneous dispersion of metallic particle[b]	Liu et al. 1999
2-Methylopentene isomerization	Higher conversion, higher selectivity	Changed dispersion of metallic particles[b]	Thiebaut et al. 1983, 1993, Seyfried et al. 1994, Roussy et al. 1997a
Methanol steam reforming	Higher production rate, higher selectivity	No explanation	Zhang et al. 2005
	Reduction in the reaction temperature	Homogeneous energy dissipation	Perry et al. 2002
	Higher conversion	Double absorption of microwaves by both the reagent and the catalyst	Chen and Lin 2010

(Table 4 Continued)

Application	Observed effect	Explanation of observed effects	References
	Higher conversion and significant spatial temperature gradients	Hot-spot formation	Durka et al. 2011
2-Propanol dehydration	Reduction in the reaction temperature	No explanation	Bond et al. 1994

[a]Effect observed only for specific catalysts.

[b]Effect observed only when catalyst was pretreated under microwave conditions.

N/A, not available.

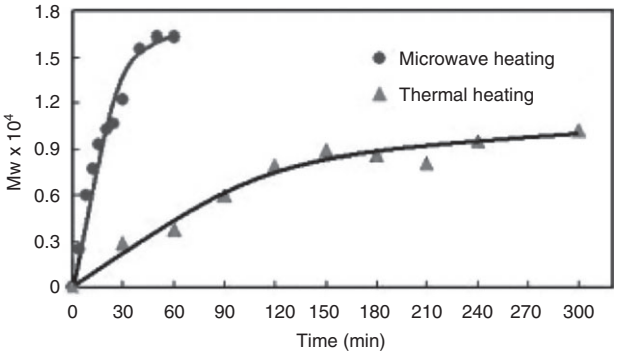

Figure 7 Molecular weight-versus-time curve for the direct polyesterification of butane-1,4-diol with succinic acid.
Reproduced with permission from Velmathi et al. (2005).

3 Microwave-assisted separation systems

The application of microwaves to different separation processes is certainly less explored compared to the application of microwaves to reactive processes. However, several striking research findings indicate that the potential of microwaves to intensify separations is at least as high as the potential of the technology for chemistry intensification. On this ground, we present in this section some important works on microwave-assisted separations including solid-liquid extraction, adsorbent regeneration, crystallization, distillation, and membrane separations.

3.1 Extraction

Any (solid-liquid) extraction process involves three common stages: material pretreatment, extraction, and conditioning of the extract. The pretreatment stage is especially important to allow the access of the extraction media to the compounds of interest inside the physical matrix (Laurent et al. 2001). Some common industrial processes of extraction of bioactive ingredients are solvent extraction, steam distillation, and supercritical fluid extraction.

3.1.1 Solvent extraction

It is based on the solubility of the desired compound into a given solvent that has to be chosen in accordance with the process suitability, sustainability, and economy. The most commonly used solvents nowadays are hexane, cyclohexane, and ethanol. Less frequently, dichloromethane and acetone are used (Lagunez Rivera 2006).

3.1.2 Steam distillation

It is the most widely used technique in the commercial extraction of essential oils (Masango 2005). The lower viscosity and higher diffusion coefficients of the vapor phase makes the extraction of volatile compounds from the porous plant material easier. On the contrary, water steam possesses a high latent heat of evaporation and is

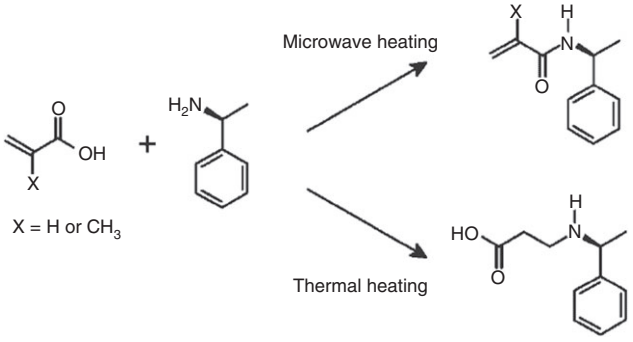

Figure 8 Influence of microwave irradiation on selectivity in the synthesis of (methyl)acrylamides.
Reproduced with permission from Hoogenboom and Schubert (2007).

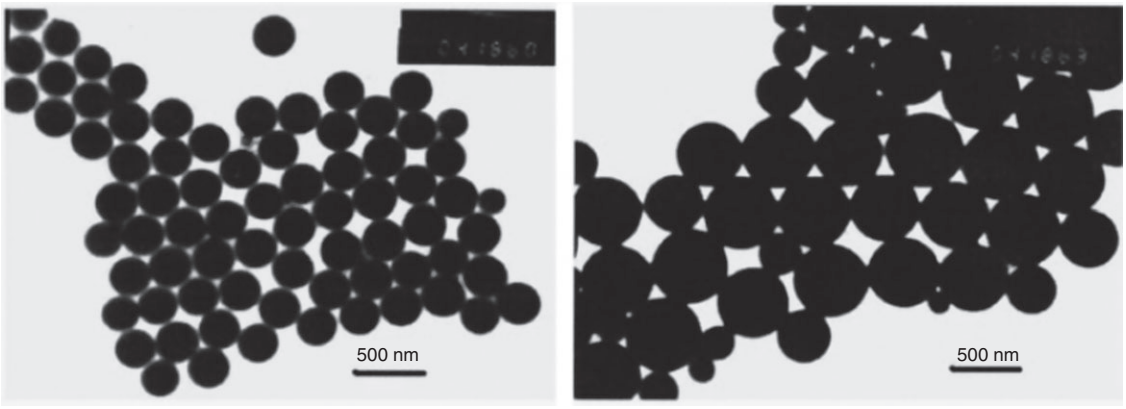

Figure 9 Images of polystyrene particles obtained in emulsion polymerization with (left) and without (right) microwave irradiation. Reproduced with permission from Xu et al. (2005).

relatively easy to obtain. Steam distillation for recovering herbaceous oils relies on bringing oil and steam into contact at a temperature close to the boiling point of water (Denny 2002).

3.1.3 Supercritical fluid extraction

Fluids at the supercritical state have solubilizing properties (e.g., density) similar to those of liquids and transport properties similar to those of gases (e.g., diffusion coefficient). The advantages of supercritical fluid extraction are higher diffusion rate of solute than in liquids, lower fluid viscosity compared to liquids, higher fluid density compared to gases, and solubilizing power can be controlled by pressure and temperature. CO_2 is widely used to extract natural products because it (1) has a low critical temperature (31.1°C) that allows the extraction of thermolabile compounds, (2) suppresses side oxidation reactions, (3) is not toxic, and (4) can have polarity similar to that of hexane (Starmans and Nijhuis 1996).

Techniques used in the extraction of valuable compounds using microwaves are mainly based on the modifications of steam distillation and solvent extraction. Thus, the reported experiments and studies use solvents, water, and steam to extract the volatiles retained in the structure of plants.

3.1.4 Microwave extraction using steam as carrying medium

This kind of extractions is mainly applied to extract volatile fractions from plants and include, among others, solvent-free microwave extraction (SFME), improved microwave steam distillation (MSD), modified hydrodistillation, and microwave accelerated steam distillation (MASD). In these processes, steam can be produced inside and outside the bed of plants (Figure 10) or just applied to a moist plant bed. Table 5 presents some applications of this kind of extraction. Most researchers use modified household microwave ovens, which makes it difficult

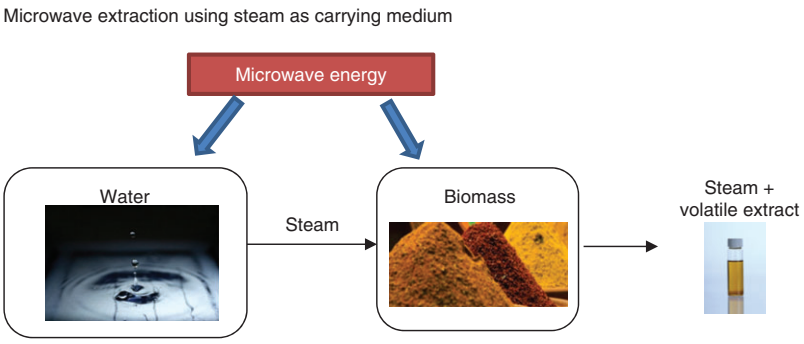

Figure 10 Representation of the extraction of essential oils with microwaves when steam is the carrying medium.

Table 5 Microwave extraction with steam as carrying medium.

Extraction technique	Plant materials	Mass of plant (g)	Moisture (%)	Microwave power (W)	Time (min)	References
SFME	Basil, garden mint, thyme	250	90, 95, and 80	500	30	Lucchesi et al. 2004
SFME	Lavandin super	100	50	600	10	Mato et al. 2008
SFME	Cardamom	100	67	390	75	Lucchesi et al. 2007
MHG	Citrus fruits	500	NR	500	15	Bousbia et al. 2009
MHG	Lavender flowers	250	Ambient dried	200	150	Farhat et al. 2009
MSD	Lavender flowers	20	Ambient dried	200	6	Sahraoui et al. 2008

SFME, Solvent-free microwave extraction; MHG, Microwave hydrodiffusion and gravity; MSD, Microwave steam distillation.

to evaluate the process in terms of the electromagnetic energy deployment.

In modified hydrodistillation, plants are fed to the extraction vessel in a water bath, and microwaves are applied to the mixture (Golmakani and Rezaei 2008). Microwave heating causes the water to reach its boiling point. At the same time, essential oils are being transferred to water in the bath (Figure 11A). The steam produced takes essential oil with it, which is condensed downstream. This method can be thought of as solvent extraction, but an additional step takes place, namely, the evaporation of water and its volatile content. An interesting modification of this method is to transfer microwaves, through an antenna, directly into the sample (Flamini et al. 2007). Experimental results report yields similar to those obtained with traditional methods with reduction in energy consumption of approximately 30%–40%.

SFME is one of the techniques that have been recently studied to extract essential oils from fresh plants (Lucchesi et al. 2004, Wang et al. 2006, Okoh et al. 2010). Here, moist plant matter (fresh or soaked in water) is introduced to a microwave cavity and exposed to electromagnetic energy (Figure 11B). Results show that the essential oil obtained contains higher amounts of valuable oxygenated compounds as a result of shorter extraction times. Time and energy consumption can be reduced by as much as 18 times (Lucchesi et al. 2004). These results are a consequence of both rapid heat delivery and trichomes rupture during microwave heating (Figure 12) (Lucchesi et al. 2007). Moreover, steam is generated inside the bed resulting in reduction in the waste generated from condensation inside the plant and in the condenser, thus enabling a greener technique. Interestingly, some methods named as microwave hydrodistillation are basically the same as

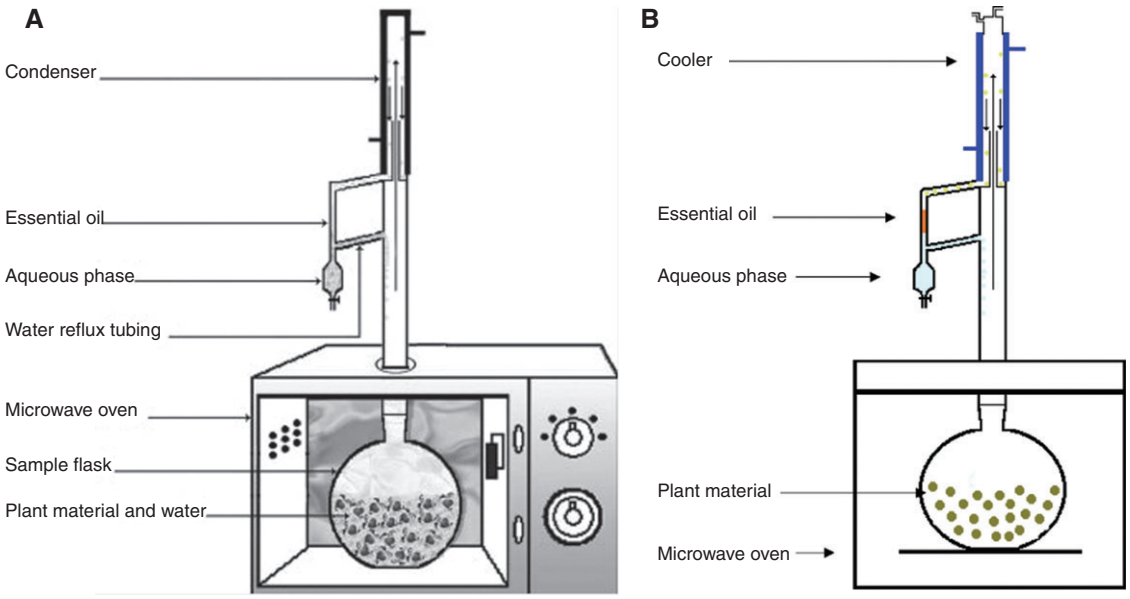

Figure 11 Setups for microwave extraction of essential oils using steam as carrying medium: (A) modified hydrodistillation (Golmakani and Rezaei 2008) and (B) Solvent-free microwave extraction.
Reproduced with permission from Lucchesi et al. (2004).

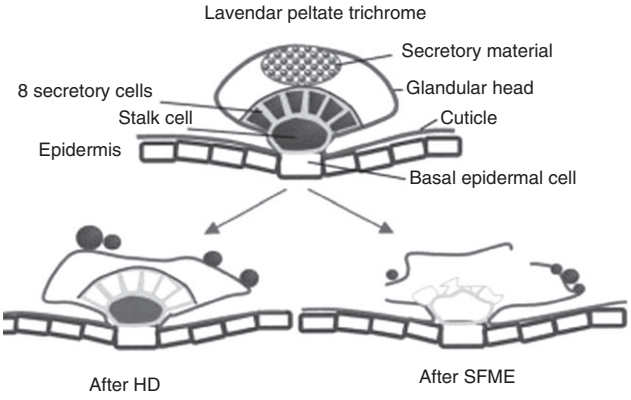

Figure 12 Effect of microwave energy on trichomes during SFME and hydrodistillation.
Reproduced with permission from Lucchesi et al. (2007).

SFME after soaking of the plants (e.g., seeds) (Lo Presti et al. 2005). A predictive model of microwave heating has been applied to this process (Navarrete et al. 2012).

MASD is very similar to steam distillation since steam is passed through a packed bed with plants, but at the same time microwaves are applied to the bed and the water container below it. This reduces the necessary time to extract the essential oil. An interesting modification is MSD, which uses the steam produced outside the microwave system while microwaves are applied to the plants bed. In this case, the energy consumed is 60 times lower than that used in steam distillation (Sahraoui et al. 2008).

Some other methods include vacuum microwave hydrodistillation, compressed air microwave distillation (Craveiro et al. 1989), and a combination of microwave hydrodiffusion and gravity (MHG) (Bousbia et al. 2009). Broadly speaking, all these methods reduce the process time and energy consumption via the aforementioned trichome breakup and more efficient heating.

3.1.5 Microwave extraction using liquid solvents as carrying media

This kind of extraction is mainly used to extract soluble natural compounds such as antioxidants (e.g., polyphenols) (Pan et al. 2003, Chemat et al. 2005, Jain et al. 2009). Table 6 presents some more applications of this kind of extraction. Water and organic solvents can be used to collect the compounds of interest. When a lossy solvent is used (e.g., water), the rapid overheating is usually responsible for the increased extraction rates (Veggi et al. 2013). On the contrary, organic solvents are poor absorbers of microwave energy, and when present, most microwave energy dissipation occurs directly in the plant structure. Once the walls of microstructures in the plants are broken, secondary metabolites (e.g., oleic acid) are easily extracted and dissolved by the surrounding solvent. This has allowed drastic improvements in time and energy consumption together with higher yields when using this technology (Chen and Spiro 1995, Chemat et al. 2005, Mandal et al. 2007).

Given that mass transfer is the rate-limiting step of the microwave-assisted extraction (MAE) process, appropriate pretreatment of the material is essential (e.g., grinding) (Rodríguez-Rojo et al. 2012). Moreover, dielectric properties have been measured in order to predict the heating profiles with the assistance of numerical modeling (Sólyom et al. 2013). Mass transfer and extraction kinetics have been proposed as well (Spiro and Soon Chen 1995, Amarni and Kadi 2010). Given that there are many studies on mass transfer phenomena in MAE, this appears to be the most suited technique currently for use at large scale. Terigar et al. (2011) reported on the development and testing of a pilot-scale 5 kW, 915 MHz focused cavity for continuous MAE of oil from soy flour and rice bran.

Table 6 Microwave extraction with solvents as carrying medium.

Product	Plant materials	Solvent	Conditions	Microwave power (W)	Time (min)	References
Polyphenols	Green tea	Ethanol/water	1 bar, 85–90°C	700	5	Pan et al. 2003
Microalgal pigments	Microalgae	Acetone	Vacuum and atmospheric pressure	25–100	3–13	Pasquet et al. 2011
Soluble proteins	Soybean	Water	60°C, 1 bar	–	10–30	Choi et al. 2006
Vegetable oils	Soybean and rice bran	Ethanol	Continuous system at 73°C, 0.6 and 1.0 l/min	Up to 5 kW	Res. time 21 min	Terigar et al. 2011
Flavonol glycosides	*Ginkgo biloba*	Ionic liquid	1 bar	120 W	15	Yao et al. 2012

3.1.6 Applications and development outlook

One common advantage when using microwave-based extraction techniques is the drastic reduction in time. This implies that the valuable compounds will not be exposed to severe conditions and therefore could retain higher activity when compared with other methods (Pan et al. 2010, Navarrete et al. 2011). Two major obstacles seem to lie in the track to wide commercialization of these extraction processes: relatively high-energy cost and lack of a unified methodology for design and scale-up. Electrical energy is the most expensive form of energy, but given the drastic time reduction reported when using microwaves the potential for a cheaper and more efficient process exists.

Recently, a study comparing batch SFME and hydrodistillation of fresh rosemary plants at laboratory and pilot scales was published (Filly et al. 2014). The pilot study was performed with 3 kg of fresh rosemary plant, which amounts to a 20-fold increase in the material load compared to the laboratory-scale study (Filly et al. 2014); microwave irradiation power was 3 kW over 30 min. An 18-fold reduction in the specific energy consumption was achieved compared to hydrodistillation. This is clearly a first step toward commercial applications. In future work, it would be interesting to compare these processes in continuous mode. Some examples of commercial equipment suitable for scale-up of MAE processes are available (Li et al. 2013).

Nevertheless, in order to make a valuable economic evaluation of the process, some kind of scale-up methodology has to be considered. This requires the generation of a database of extraction kinetics and microwave conditions, as determined by numerical models, in order to obtain correlations based on dimensionless numbers, where the dielectric properties of the material under treatment should make an essential part (Takhistov 2007).

An interesting approach is proposed by Chan et al. (2013), where extraction is parameterized as a function of the absorbed energy density with independent parameters for the microwave exposition and the extraction kinetics (Figure 13) (Chan et al. 2013). This method can even be adjusted for models for microwave extraction by means of steam (Navarrete et al. 2010).

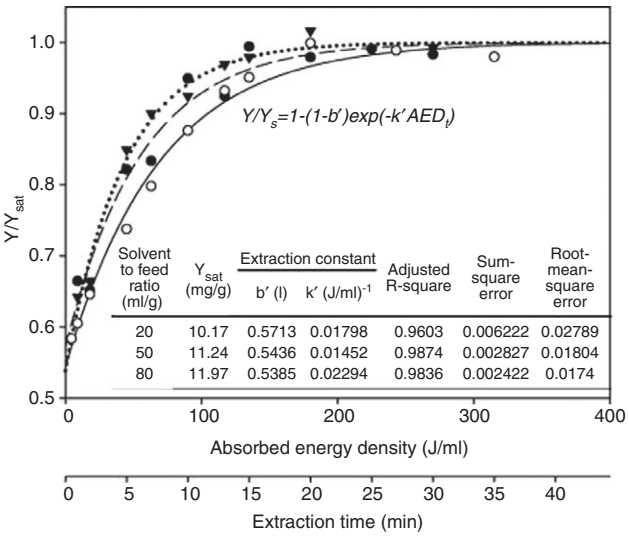

Figure 13 Typical extraction curve adjusted by the model proposed by Chan et al. (2013).
Reproduced with permission from Chan et al. (2013).

3.2 Adsorbent dehydration/regeneration

The conventional thermal dehydration and regeneration of adsorbents, mainly zeolites and activated carbons, from volatile organic compounds (VOCs) and hazardous air pollutants (HAPs) are time-consuming and energy-expensive processes in the chemical industry. In this frame, microwave-assisted desorption has been researched as an alternative due to the specific heating characteristics of microwaves, including fast volumetric heat transfer and selective interaction with polar adsorbed compounds.

Extensive reviews of the field of microwave-assisted desorption until 2009 are given by Yuen and Hameed (2009), focusing on activated carbons, and by Cherbanski and Molga (2009). Shorter desorption times and potential for energy savings, volumetric footprint reduction, and downstream simplification of adsorbate separation are reported as the main advantages of application of microwave energy. After 2009, Cherbanski et al. (2011) presented a comparison of microwave swing regeneration and temperature swing regeneration of 13X molecular sieves in terms of desorption kinetics of a polar (acetone) and a nonpolar (toluene) component. It was found that microwave swing regeneration runs much faster even when the adsorbent temperature is much lower than the gas temperature in the case of temperature swing regeneration. The observed enhancement of microwave-driven desorption was more pronounced for the polar adsorbate. The effect of selective microwave-adsorbate interaction was also discussed by Kim and Ahn (2012). They found that microwave heating resulted in higher desorbed amounts of methylethylketone and toluene from MS13X and HY901 zeolites compared to conventional heating, with the amount of methylethylketone being higher than that of toluene due to the different dielectric constant values of the two compounds. Chowdhury et al. (2012) studied the desorption

of ethylene/ethane and carbon dioxide/methane mixtures from Na-ETS-10 (titanium silicate molecular sieve) under microwave and conductive heating. Higher gas recovery at three times lower process time and one order of magnitude lower specific energy consumption is reported for the case of microwave heating. Moreover, the adsorption capacity of Na-ETS-10 remained unchanged after five adsorption-regeneration cycles for both heating modes. In the same context, Foo and Hameed presented several studies in 2012 on microwave-assisted desorption of methylene blue from activated carbons prepared from different materials (Foo and Hameed 2012a,b,c). The focus was on characterization of the properties (pore structural analysis, zeta potential measurement, and surface acidity/basicity) of the original and regenerated activated carbons. After five successive adsorption-regeneration cycles, the activated carbons preserved their porous structure and adsorption capacity. Another study by Caliskan et al. (2012) explored the regeneration of activated carbons saturated with the pharmaceutical compound promethazine using microwave and electric heating. In contrast with most experimental results in the literature, the authors found that the adsorption capacity decreased after successive adsorption-desorption cycles. This was due to the thermal cracking of the adsorbate, which was more pronounced under microwaves (Caliskan et al. 2012). Their results imply that the regeneration efficiency depends on the nature of the adsorbate and the operating conditions.

Collectively, the potential of microwaves to intensify adsorbent regeneration processes has been shown at laboratory scale and agreed upon by many researchers. However, valorization of the technology will depend on the overall energy efficiency compared to conventional heating. As rightly concluded by Cherbanski (2011), this necessitates proper microwave engineering and careful process design.

3.3 Crystallization

Although there are numerous experimental papers on microwave-assisted chemical synthesis of nanoparticles in solvents, there are only few papers on the application of microwaves to evaporative crystallization. Pinard and Aslan (2010) used microwave-assisted evaporative crystallization to glycine molecules on silver nanoparticles coated on a glass surface. The metal nanostructures are meant to serve as selective nucleation sites and as a microwave transparent medium to create a temperature gradient between the solvent (aqueous phase) and the nanostructures. The postulated temperature gradient is assumed to accelerate the mass transfer of glycine molecules from the solution to the nanoparticles and thereby nucleation. In addition, microwaves were used to speed up evaporation. Collectively, it was reported that the application of microwaves induced multifold decrease in the total crystallization time compared to conventional evaporative crystallization at room temperature. The metal-assisted and microwave-assisted evaporative crystallization has been applied by the same group to L-alanine (Alabanza and Aslan 2011, Alabanza et al. 2012) and L-arginine (Pinard et al. 2012) as well.

Recently, Radacsi et al. (2013) presented a study on the effect of evaporation rate on the crystal size. In this context, niflumic acid was crystallized from ethanol solutions by microwave heating in a single-mode cavity and by conventional (conductive) heating using a heating plate. The final product size, as measured by a particle size analyzer, was reduced when increasing the evaporation rate using microwave irradiation. In the event of microwave heating, heat transfer does not depend on the thermal conductivity, which is low for conventional solvents, such as water, methanol, or ethanol (Assael et al. 1989). In contrast, it depends on the dielectric properties of the solution. Polar solvents, such as water and alcohols, have very high loss tangent (tan δ) (Metaxas 1996), a measure of inherent dissipation of electromagnetic energy of the material, enabling rapid volumetric heat transfer and solvent evaporation. Higher solvent evaporation rates in the event of microwaves result in shorter crystallization times (the time window between the time at which the solution becomes supersaturated and the time of complete solvent evaporation) and thus to smaller crystals due to higher supersaturations (Figure 14). Finally, X-ray diffraction showed that neither the microwave irradiation nor the hot plate-aided evaporative crystallization altered the crystal structure of NIF compared to that reported in literature (Radacsi et al. 2013).

3.4 Distillation

When accounting the scale and importance of distillation and reactive distillation in the process industry, any improvement in the reaction and/or separation functions could have a wide application and direct impact on large-scale operations. In this context, Altman et al. (2010) experimentally explored the effect of microwaves on the separation of binary mixtures by comparison with conventional thermodynamic equilibrium experiments. Although the effects of electromagnetic radiation on boiling and evaporation have been studied for more than

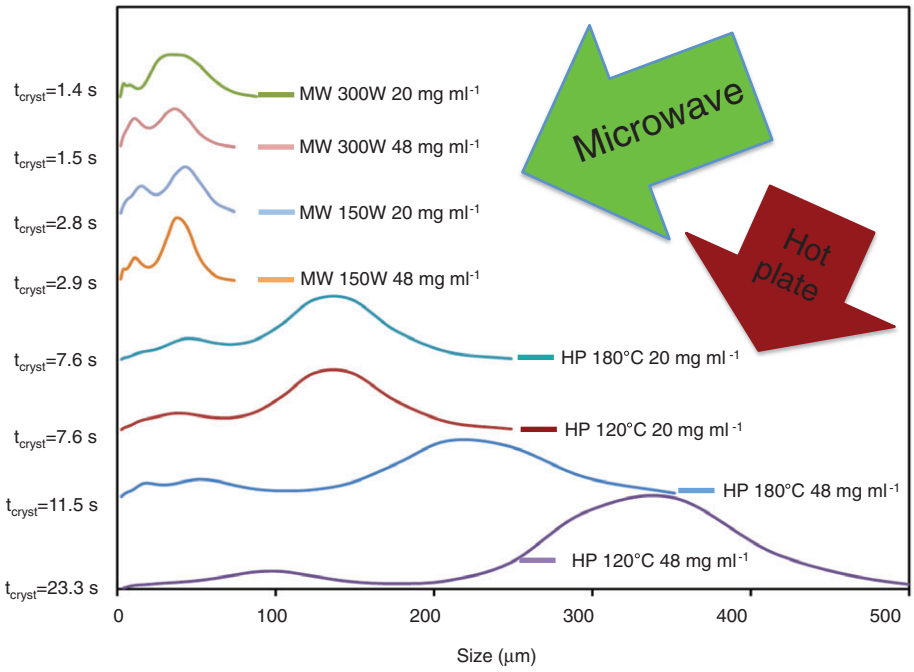

Figure 14 The crystal size (volume-based mean diameter) and the crystal size distribution width decrease with decreasing crystallization time (t_{cryst}).
Reproduced with permission from Radacsi et al. (2013).

30 years, the underlying physics are not yet universally agreed upon. Different explanations put forward include the surface hydrodynamic instabilities (Courville et al. 1991, Stuerga and Lallemant 1993a,b, 1994, Stuerga et al. 1994), superheating (Chemat and Esveld 2001), nonequilibrium conditions at the evaporating interface (Thiebaut et al. 1983), and pressure increase at the interface (Roussy et al. 1983). According to Altman et al. (2010), conventional vapor-liquid equilibrium (VLE) experiments were performed using binary mixtures of the components involved in the esterification synthesis of n-propyl propionate from propanol and propionic acid. VLE experiments were carried out under microwave heating as well to investigate the potential changes in phase composition compared to conventional VLE (Altman et al. 2010). The reason for such a composition change can be one of the effects mentioned above or the different interaction of microwaves with the binary components according to their dielectric properties. It was found that, for the binaries under consideration, the vapor phase was richer in the lower boiling temperature component in the event of microwave heating. The extent of separation enhancement varied among the different mixtures tested depending on the difference in the boiling points of the mixture components and on their dielectric properties (Figure 15) (Altman et al. 2010).

In terms of a real separation process in a distillation column, the results above imply the potential for smaller columns with a reduced number of trays to achieve a certain separation efficiency in comparison to the conventional adiabatic column design with heat exchange only in the reboiler and condenser. However, technical solutions should be sought as regards (1) the way to bring microwaves into a distillation column (design of hybrid microwave distillation hardware) and (2) the uniform irradiation of the large vapor-liquid interface over a tray.

Very recently, a similar kind of study was carried out by Gao et al. (2013) using the ethanol/benzene and iso-octanol/bis(2-ethyhexyl)phthalate (DOP) binary mixtures, which confirmed that the application of microwave irradiation can shift the VLE obtained under conventional heating. In particular, it is reported that, in the case of the ethanol/benzene binary, the change in the VLE increased with increasing field strength (power applied) until a plateau value. The authors speculate that this is due to the higher rate of microwave absorption of ethanol (strong microwave absorber) compared to the rate of heat transfer from ethanol to benzene (weak microwave absorber). On the contrary, the authors report no microwave effect in the case of the iso-octanol/DOP system, which they attribute to the close dielectric constant values of the two components.

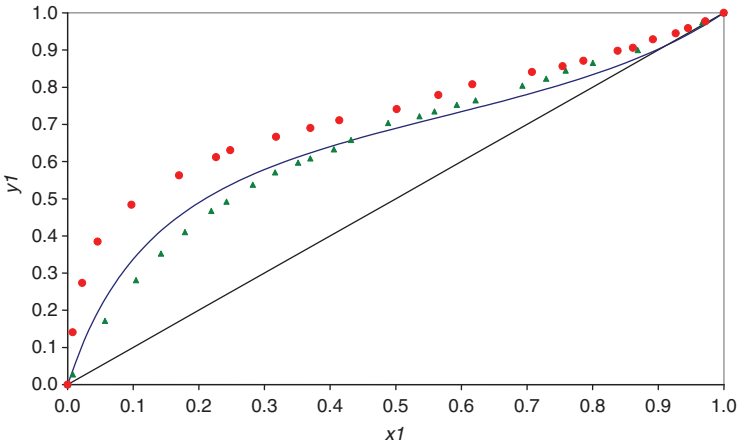

Figure 15 xy graph obtained with a single-mode microwave oven and a custom-designed distillation head.
Binary system: propanol (1)/n-propyl propionate (2). (-) UNIFAC, (▲) experimental data set without microwaves, and (•) experimental data set with microwaves. Reproduced with permission from Altman et al. (2010).

3.5 Membranes

Microwave irradiation has extensively been used as a tool for the synthesis of various membrane materials (Tompsett et al. 2006, Li and Yang 2008, Patete et al. 2011). In contrast, there have been only few research reports on the application of microwaves to membrane separation processes, where it has been shown that microwave irradiation may intensify gas permeation and membrane distillation processes. It has been postulated that the selective interaction of microwaves with polar functional groups of polymeric membranes and/or with the feed mixture components can accelerate diffusivity and permeability through the membrane.

Nakai et al. (2006) investigated gas permeability through hydroxypropyl cellulose (HPC), cellulose triacetate (CTA), and poly(methylmethacrylate) (PMMA) membranes under microwave irradiation in comparison with the permeability obtained with conventional heating. They found higher permeability coefficients for several gases under microwave irradiation. The effect was attributed to the accelerated molecular motion of -OH and -COO- group moieties in the membranes under microwave irradiation. Similar results were reported by Nakai et al. (2005) with cellulose acetate (CA) membranes also containing polar functional groups. On the contrary, no effect in gas permeability was observed by the same authors in the case of a polystyrene membrane having no functional groups.

Finally, Ji et al. (2013) performed vacuum membrane distillation experiments using polyvinylidene fluoride (PVDF) hollow fiber hydrophobic membranes containing nonpolar functional groups. They observed mass transfer enhancement with microwaves most likely due to decrease in temperature polarization, with no significant effect on the mechanical properties and hydrophobicity of the membrane materials.

4 Challenges and new concepts in design and scale-up of microwave-based processing systems

Aside from the chemistries discussed in the previous sections, parallel development into microwave processing equipment is currently ongoing. As mentioned in Section 1.3, two types of system are often used for microwave chemistry: multimode and single-mode cavity systems. The popular off-the-shelf solutions include domestic microwave ovens, purpose-built laboratory multimode cavity systems (Milestone SRL 2009, Sineo 2009, CEM 2011b), and predominantly the CEM Discover Microwave Synthesis System (CEM 2011a) as a single-mode system. From a practical point of view, these systems enable fast, clean, and convenient heating for laboratory use. It must be noted that, for many applications, these systems suffice and also that they could prove a valuable stepping stone for developing microwave-enhanced chemistries. They certainly have their limitations, though. The work in our group (Sturm et al. 2012, 2013b, 2014) has shown that the microwave field spatially distributes nonuniformly in complex interference patterns with a high sensitivity to parametric variations. As such, the main disadvantages of off-the-shelf resonant microwave cavity systems are listed as follows.

- In these systems, the local properties of the electromagnetic field in terms of field strength, field orientation, and polarization for practical purposes can neither be predicted nor controlled. It is therefore impossible to quantifiably correlate an observed effect on the process performance with the microwave field. Consequently, the outcome of experiments is likely to be affected by the parameters specific to the devices used. Reproducibility is therefore difficult to achieve between different types of equipment.
- Aside from the inherently nonuniform and difficult to predict morphology of the microwave field, there are also no means to manipulate and optimize its spatial application. Consequently, any benefit microwave fields may have over the conventional process activation cannot be harnessed to its full potential.
- Further, there are no monitoring sensors for forward and reflected microwave power nor are there arrangements for the minimization of the latter power transmission (i.e., so-called impedance transformers or matching circuits) (Roussy and Pearce 1995, Meredith 1998). As a consequence, low utilization of microwave energy and low overall energy efficiency are likely to occur.
- Finally, none of these systems can operate outside of the 2.45 GHz ISM band (ITU 2004). Microwave activation at other frequencies remains therefore largely unexplored.

Aside from the development of chemistries, the microwave-enhanced process equipment needs to be developed in order to achieve successful industrial application of microwave fields in chemical processes. The grand challenge in this respect is to design equipment that integrates both the processing and electromagnetic aspects into one system to alleviate the challenges mentioned above. Such systems would permit microwave fields to be transmitted efficiently into the process and to be distributed over the process media according to a set of predetermined requirements. In this section, we highlight several developments that could lead to such processing systems. It is remarked, however, that these developments are by no means a complete overview of the systems that could be considered for microwave processing.

4.1 Internal transmission line systems

One current development is being commercialized by SAIREM (a microwave and radiofrequency technology provider). They launched a new range of integrated reactor and microwave transmission systems under the generic name LABOTRON (Radoiu et al. 2009, SAIREM 2010). This range of systems is especially designed to carry out microwave-assisted synthesis and extraction processes in batch or in continuous flow both at laboratory and pilot scale. The novelty in this type of equipment, as opposed to conventional single-mode or multimode cavity types, lies in the use of an internal transmission line that selectively brings energy directly inside the process fluids. SAIREM offers the LABOTRON equipment as a solution for a wide area of chemical processes ranging from a few grams per hour to more than 1 kg h^{-1}. In addition, the working principle is said to facilitate the scale-up of microwave-assisted multiphase processes in both batch and continuous flow modes. Two types of reactor/applicator systems are available (Figure 16).

1. Batch reactor with volumes from 1.5 to 20 l. A 100-liter scaled-up version is currently under development. The reactor is made of stainless steel and is equipped with a cooling jacket and a mechanical stirrer.
2. Continuous-flow helix type of reactor mounted on a U-shaped waveguide. The available internal volumes range from 40 to 150 ml.

In these systems, a microwave field is fed via a U-shaped waveguide and transmitted into the reactor via the internal transmission line that is placed in the middle of the reactor in direct contact with the reaction mixture. SAIREM lists a number of advantages: the internal transmission line helps overcome the penetration depth limitation, the system is adaptable for specific processing needs in terms of volume and batch versus continuous operation, high power density, and efficient cooling via a cooling jacket.

In addition to these improvements, as opposed to typical off-the-shelf microwave systems for laboratory use, industrial and application-tailored microwave systems,

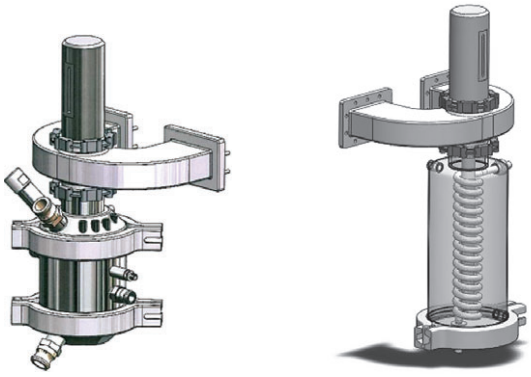

Figure 16 Batch reactor and SPIN M (right) continuous-flow reactor mounted on the LABOTRON microwave processing system.

such as the LABOTRON range, incorporate arrangements for monitoring and control of forward and reflected power. This allows for minimization of the reflected microwave power and thereby enables a high utilization efficiency of microwave energy.

4.2 Coaxial traveling microwave reactor

Another development in microwave processing equipment design is currently being investigated in our group. It aims at engineering microwave fields to activate chemical processes under conditions that are tailored and controlled according to a predetermined set of requirements. This could involve macroscale optimization of spatial and temporal heating patterns or microscale optimization of selective microwave-matter (e.g., catalyst and molecules) interactions.

As was mentioned in Section 1.3 and at the beginning of Section 4, resonant fields limit the spatial control over microwave fields. The interference that occurs in the microwave field of constructively and destructively combining waves causes the electromagnetic activation to be distributed nonuniformly in patterns that are difficult to predict and control (Chow Ting Chan and Reader 2000, Sturm et al. 2012, 2013b, 2014). An alternative approach is presented here, which is based on the use of traveling electromagnetic waves as opposed to standing electromagnetic waves as an unconventional means of thermochemical activation. Traveling electromagnetic waves do not occur in confined spaces. They travel through a medium toward one direction without being reflected by reflective surfaces, such as the cavity walls. As they move, a part of the electromagnetic energy is dissipated for process activation, according to the dielectric properties of the medium, and the remainder of the energy is transported downstream. Due to the absence of interference between the traveling waves incident toward one direction and reflected portions of these waves in the opposite direction, resonant standing-wave patterns arising from superposition of interfering waves do not occur. Contrary to resonant standing-wave fields, nonresonant traveling-wave fields can be precisely controlled and optimized according to different objectives for chemical reactor activation. A concept study is presented here on the design and optimization of a coaxial traveling microwave reactor (TMR) for activation of heterogeneous gas-phase catalytic reactions.

Figure 17 shows a photograph of a typical coaxial cable. It consists of two concentric conductors with dielectric filler between them. The reactor design is based on

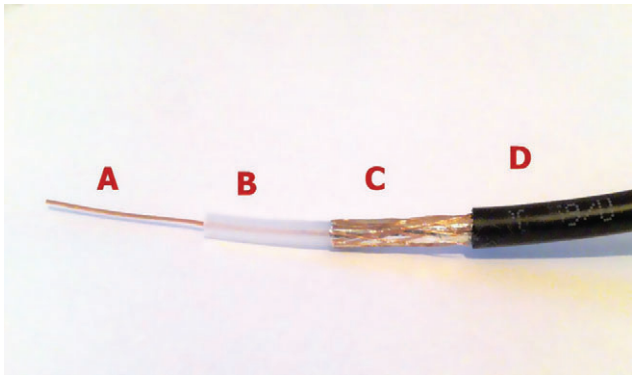

Figure 17 RG-59 coaxial cable.
It consists of an inner conductor (A), a dielectric filler (B), an outer conductor (C), and an outer insulator (D).

this waveguide type; it has two concentric conductors – inner and outer – and a microwave field travels between these conductors in one direction along the reactor. In the coaxial TMR concept, the process fluids flow between the conductors and are exposed to the microwave field for activation of the process. An important aspect is the geometrical optimizability of the reactor to allow for energy distribution over the reactor volume according to a predetermined set of requirements.

The reactor concept presented herein is shown in Figure 18. The focus in this concept lies in the selective catalyst heating. This is, in principle, beneficial not only in terms of energy savings, as the inert parts of the reactor are not directly heated, but also in terms of chemical efficiency, as undesired side-reactions in the bulk phase may be suppressed. The space between the inner and outer conductors contains a dielectric material and a monolithic (cordierite/silica) multichannel layer adjacent to the outer conductor. The channels' volume will be occupied by the gas phase. The channel walls transverse to the outer conductor will be functionalized with metal catalyst.

A two-step approach toward optimization is employed. First, the cross-section is optimized; the goal

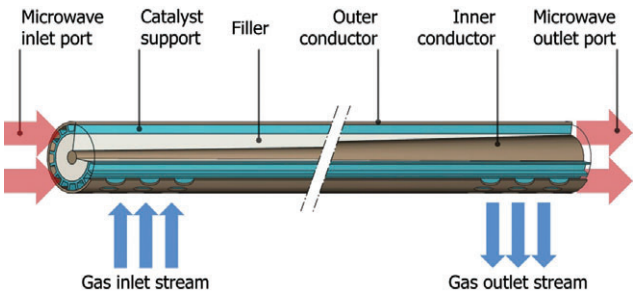

Figure 18 Coaxial traveling microwave gas phase monolith reactor concept.

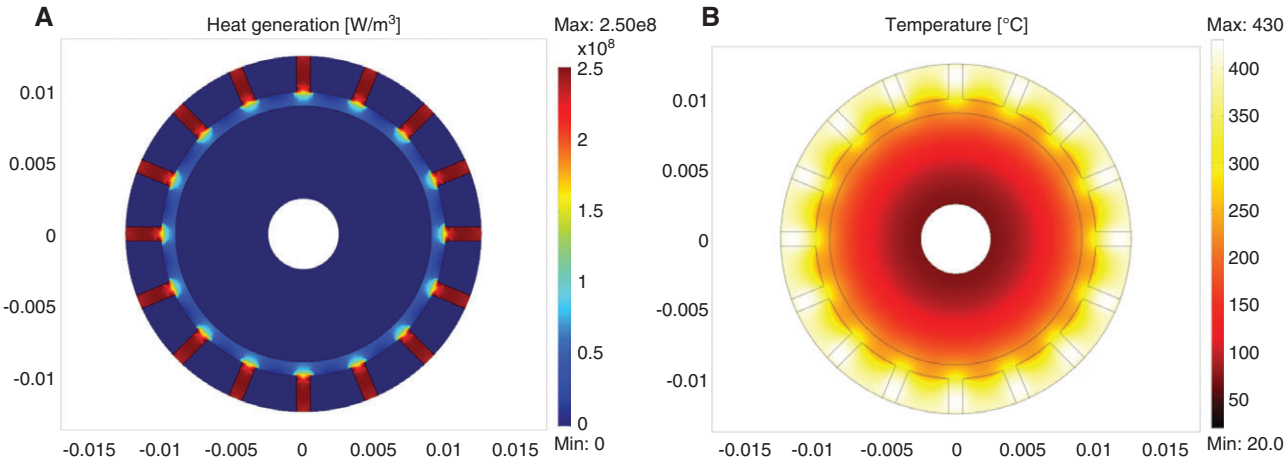

Figure 19 Simulation of the heating rate distribution (A) and temperature (B) over the cross-section of the coaxial traveling microwave monolith reactor for gas-phase heterogeneous catalysis.
The temperature field corresponds to 12 s of microwave exposure.

here is to "focus" the electric field on the metal nanoparticles (selective/direct catalyst heating) in the monolith walls. Due to the filler material having a higher permittivity compared to the effective permittivity of the outer monolithic layer containing the gas phase, the electric field is "pushed" toward the outer conductor. The densified field in the monolithic layer results in evenly distributed and focused heating of the transverse channel walls as shown in Figure 19.

In a second step, the profile of the inner conductor diameter is optimized along the axial direction of the reactor. As the microwave field travels down the reactor, it loses energy. Consequently, if the reactor cross-section is unchanged along its length, the electromagnetic dissipation attenuates (decays) along that direction. This would lead to lower temperatures in the downstream section of the reactor and, consequently, a reduction in the effective reactor length. In order to fully harness the benefit of microwave activation, microwave energy has to be distributed uniformly in the axial direction. This can be achieved by having an increasingly larger inner conductor diameter as the microwave field travels further downstream. This pushes the microwave field increasingly more strongly toward the outer conductor and into the functionalized catalytic walls, thus compensating for the attenuation.

Figure 20 presents the axial heating rate distribution along the reactor length both for the constant and the optimized inner conductor diameter profile. The dashed line in Figure 20 shows the heating rate for the constant inner conductor diameter, while the solid line corresponds to the optimized inner conductor diameter profile. The former indeed shows a decaying trend, while the latter shows that the heating rate along the 400 mm distance remains almost invariant. In addition to this, in the latter case, more than 70% of the microwave power at the inlet has been absorbed along the way (not shown). The microwave energy utilization may be further improved by looping the microwave energy exiting the reactor back to the inlet.

Although unsupported by experimental verification, an important message reads from this study: *locally tailored heating patterns at macro- and microscale can be achieved in TMRs* through optimization of the channels' cross-sectional geometry, the inner conductor diameter as function of length, and the filler material permittivity. This can be achieved neither with conventional heating, nor

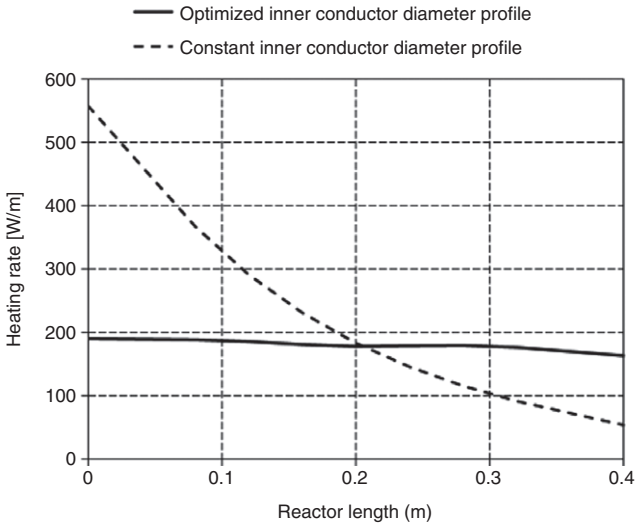

Figure 20 Axial heating rate distribution for both the constant inner diameter profile and the inner diameter profile that is optimized for a constant axial heating rate distribution.

with conventional microwave equipment used for chemical processing. In addition there is, in principle, no limitation to the length of the reactor, so the TMR concept may provide a path to the scale-up of microwave-assisted processes.

4.3 Rectangular waveguide-based systems

An important class of systems that is emerging are resonant cavities that are constructed out of standard-sized rectangular waveguides. As an example, Figure 21 displays some standard WR-340 waveguides that are used with the 2.45 GHz ISM band. Figure 22 indicates the parts that such cavity systems are typically constructed from. These parts are outlined as follows:

- A *microwave generator* that allows continuous variation of its output power.
- An *isolator* that permits microwave fields to pass in the forward direction but absorbs them in the reverse direction so as to prevent reflected microwave fields from reaching and possibly damaging the generator.
- An *impedance transformer* – also called "matching circuit" – that can be tuned to influence the microwave field such that it is not reflected out of the cavity applicator.
- A *cavity applicator* in which the process system is placed to be exposed to the resonant microwave field.
- A *variable reflector* to move and position the resonant standing-wave pattern in the cavity system.

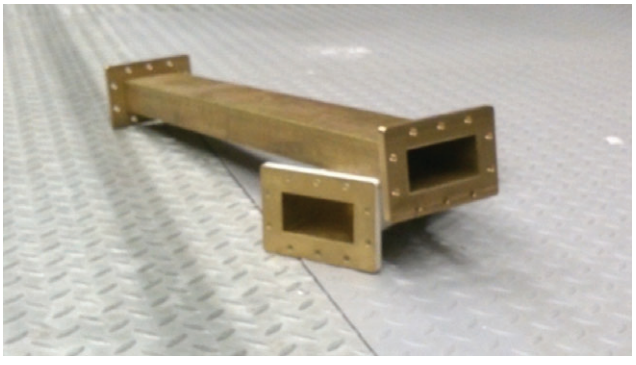

Figure 21 Standard-sized WR-340 rectangular waveguide sections.

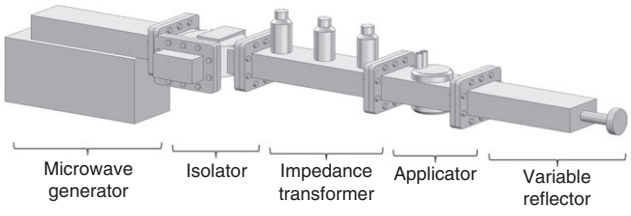

Figure 22 Typical configuration of a rectangular waveguide-based microwave system.
Refer to the text for the description of the parts and their functions.

These systems have a few notable advantages. A recent work in our group (Sturm et al. 2013a) showed that they enable experimentation with a morphologically simple and predictable microwave field and that systems based on these waveguides allow for adaptable process conditions. Moreover, this type of cavity system has already been used in a number of studies for chemical activation with microwave fields (Toukoniitty et al. 2009, de Castro et al. 2012, Patil et al. 2012).

4.4 Lower frequencies and scaling

Industrially, electromagnetic heating often involves radiofrequency heating rather than microwave heating. In principle, radiofrequency fields differ from microwave fields in their frequency and wavelength. Due to the much larger wavelengths relative to the equipment dimensions, interference patterns need much more space to emerge over. Field nonuniformity is therefore much less of an issue. Very different types of applicators are required, though, because cavities would grow to impractical sizes for these long wavelengths. Typical radiofrequency field applicators are electrodes or coils used, for example, in wood gluing presses and case hardening of steel, respectively (Brown et al. 1947). Although, in the case of microwave fields, these applicator types would need to be scaled down to match the much shorter wavelengths, they could inspire small or microstructured microwave-enhanced processing systems.

In a similar vein, scale-up of microwave systems can be realized by scaling the wavelength and equipment dimensions to the same factor. If, for example, one would lower the frequency to the 915 MHz band, which is the nearest ISM frequency band under the 2.45 GHz band, then all dimensions are scaled to a factor of 2.68 with respect to a system operating at 2.45 GHz. This would result in a 19-fold volumetric increase with the same, but scaled-up, distribution of the microwave field.

5 Conclusions

Two distinct characteristics of microwave heating, namely, rapid heat transfer/generation and selective heating, have

the potential to intensify many classes of reaction and separation processes of industrial relevance. A broad range, but not the complete list, of these processes, which are discussed in the present review, include liquid-phase organic syntheses, gas-solid catalytic reactions, polymerizations, extraction, distillation, crystallization, membrane separation, and adsorbent regeneration/dehydration. We would like to stress the potential of microwaves to intensify various chemical separations, as this has attracted less attention compared to the field of chemical reactions.

The widespread implementation of the technology at commercial production scale will ultimately depend on a number of factors, such as the energy (electricity) cost, the energy utilization efficiency, the scalability potential, and the relative benefit that microwave application will bring to the process compared to the conventional process (i.e., extent of PI). With the exception of electricity cost, the other factors are inherently linked to process design and the possibility for process control and optimization. In this context, the design of microwave equipment as an integral or modular part of process equipment is of high importance.

As far as microwave equipment is concerned, the concepts highlighted in Section 4 show that the microwave equipment for application in chemical processing does not have to be limited to the common microwave cavity systems currently used in research. Microwave equipment developments are ongoing, ranging from the commercial to the conceptual stage. There are many concepts outside the direct neighborhood of chemistry and chemical engineering that may serve as a basis for design of integrated microwave-assisted processing systems. Drawing from this expertise could point the way in the development of the truly integrated and optimal microwave processing systems.

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Graphical abstract

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A helicopter view of microwave application to chemical processes: reactions, separations, and equipment concepts

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Review: A helicopter view of microwave technology application to various reaction and separation processes, including liquid-phase organic syntheses, gas-solid catalytic reactions, polymerizations, extraction, distillation, crystallization, membrane separation, and adsorbent regeneration/dehydration is presented.

Keywords: microwaves; process intensification; reactions; separations.